



growth into larger particles by coagulation. Ultrafine particles also serve as nuclei for condensation of vapors. Thus, ultrafine particles grow rapidly by coagulation and condensation, into the accumulation mode. For these reasons, the mass of ultrafine particles in the ambient atmosphere is generally much smaller than that of the accumulation mode, where removal rates of particles reach a minimum in non-cloud conditions. The result is that in ambient conditions, the ultrafine mode is generally indistinct or absent from mass or volume profiles of aerosol particles versus size. However, a distinct ultrafine mode below $0.1\ \mu\text{m}$ diameter has been observed in quasi-ambient samples taken close to combustion sources. In these cases, the distinct ultrafine particle mode is referred to as the nuclei mode (Whitby, 1978).

While there is consensus that ultrafine metal particles are produced and emitted into the atmosphere, there is little information on ambient concentrations of ultrafine metals. The few direct measurements available can be extended with some confidence using indirect methods; i.e., from particle counting techniques that have size information but no chemical information, or from filter collection methods that have limited size information but detailed compositional information. Nevertheless, it is clear that more data on ultrafine metals are urgently needed to gain confidence in the spatial and temporal concentration profiles of this key atmospheric component.

6.9.2 Formation of Ultrafine Particles

Nucleation theory establishes that high temperature processes are generally required to form ultrafine metallic aerosols. Such processes are usually anthropogenic, although natural fires, volcanic eruptions, and other such events can contribute to ultrafine transition and heavy metals in some circumstances. Table 6-6, taken from Seeker (1990), gives the vaporization temperature of EPA-regulated metals (Federal Register, 1986) as a function of temperature, with and without chlorine available in the combustion process.

Note the dramatic shift in temperature for several elements, including lead, for the chlorine-rich combustion scenario. A similar process has been used to prevent lead from coating surfaces in internal combustion engines using leaded gasoline. The process used

TABLE 6-6. REGULATED METALS AND THE VOLATILITY TEMPERATURE

Metal	With No Chlorine		With 10% Chlorine in Waste	
	Volatility Temp. (°F)	Principal Species	Volatility Temp. (°F)	Principal Species
Chromium	2935	CrO ₂ /CrO ₃	2930	CrO ₂ /CrO ₃
Nickel	2210	Ni(OH) ₂	1280	NiCl ₂
Beryllium	1930	Be(OH) ₂	1930	Be(OH) ₂
Silver	1660	Ag	1160	AgCl
Barium	1560	Ba(OH) ₂	1660	BaCl ₂
Thallium	1330	Tl ₂ O ₃	280	TlOH
Antimony	1220	Sb ₂ O ₃	1220	Sb ₂ O ₃
Lead	1160	Pb	5	PbCl ₄
Selenium	605	SeO ₂	605	SeO ₂
Cadmium	417	Cd	417	Cd
Osmium	105	OsO ₄	105	OsO ₄
Arsenic	90	As ₂ O ₃	90	As ₂ O ₃
Mercury	57	Hg	57	Hg

Source: Seeker (1990).

chlorine and bromine-containing additives to form compounds such as PbBrCl which are gaseous at combustion temperatures but form ultrafine particles after leaving the vehicle.

Numerous theoretical and laboratory studies have shown that the typical size of metals derived from combustion is ultrafine (Friedlander, 1977; Senior and Flagan, 1982; Seeker, 1990). Analysis of particles from coal combustion by Natusch and Wallace, 1974 and Natusch et al., 1974 showed an additional aspect. There is a tendency for the condensing metal vapors to form relatively uniform thickness surface coatings on more refractory particles present in the combustion effluent stream. If the particles upon which the metals coat themselves are crustal, as in coal fly ash, this results in a final particle whose enrichment factor compared to crustal averages depends upon the initial size of the refractory particle—minor for large particles, extreme for ultrafine particles (Davison et al., 1974). This result also places the (potentially) toxic metals on the biologically-accessible surface.

Thus, the presence of metals in a combustion process such as incineration of biological and chemical wastes or treatment of contaminated soils poses a problem. Raising the temperature of

combustion high enough to completely (> 99.99%) destroy the biological and chemical species will also enhance the volatilization of metallic components in the feed stock, requiring more efficient removal methods for ultrafine and accumulation mode metals. Figure 6-95 shows the enhanced volatilization of metals as the combustion temperature is raised from 1000 °F (540 °C) to 1800 °F (980 °C) (Seeker, 1990).

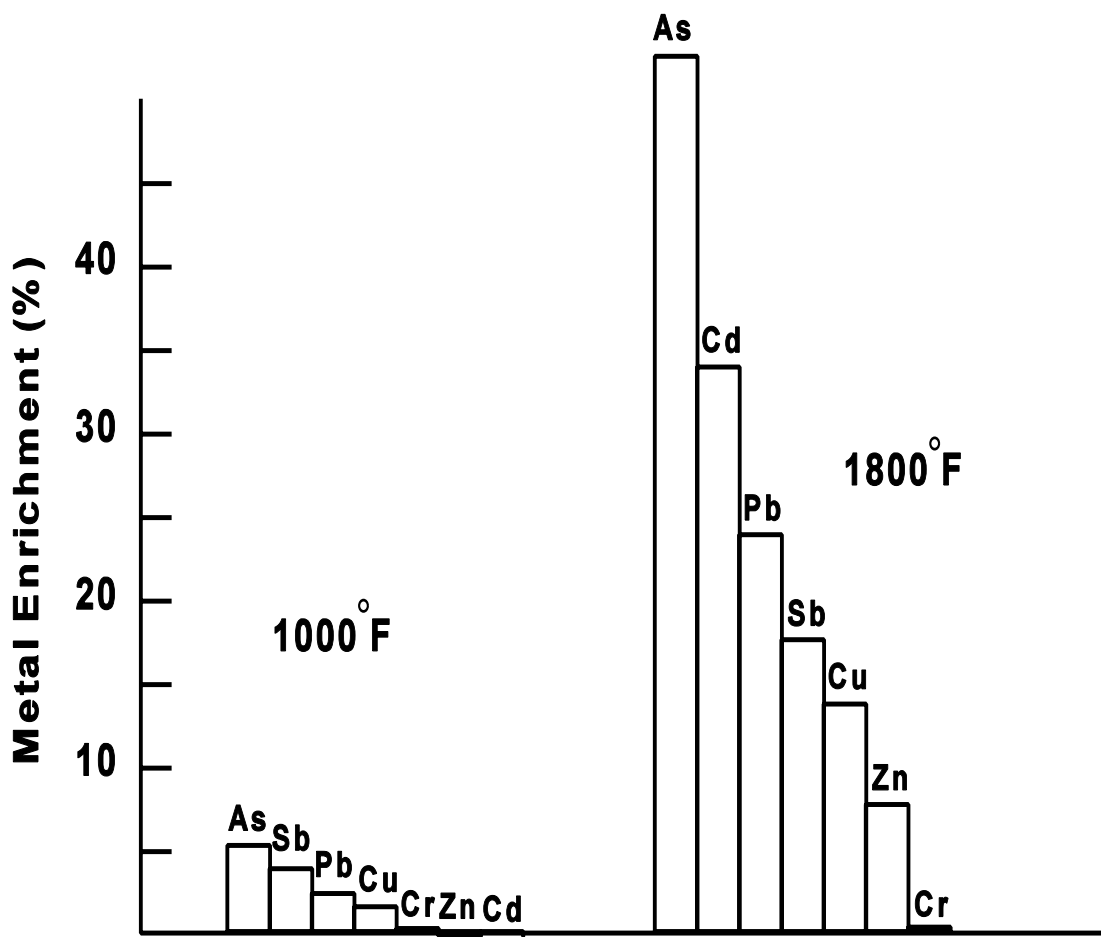


Figure 6-95. Impact of treatment temperature on the enrichment of metals in the fly ash after the thermal treatment of soils from a Superfund site.

Source: Seeker (1990).

The combustion effluent can be partitioned into three components (Seeker, 1990; Barton et al., 1990); emitted (as fly ash), captured (assuming there is an attempt to capture fine particles), and collected in the bottom ash. Assuming no particle removal equipment is in place on the combustion process, emitted particles will include both the "emitted" component and most of the "captured" component. In an uncontrolled incineration facility, 96% of mercury, 88% of cadmium, 58% of lead, and 11% of copper might be emitted into the atmosphere. If control is attempted, the capture efficiency is only 25% for mercury, but is better for most other metals, ranging from 86% for cadmium to 91% for copper (Barton et al., 1990). In addition, the chemical state of the metals in the ultrafine mode can vary from the more toxic phases (for example, arsenite versus arsenate) as a function of combustion conditions (Chesworth et al. 1994). Thus, we must expect that ultrafine metallic components will be emitted from high temperature processes in both toxic and less toxic forms.

6.9.3 Techniques for Collecting and Analyzing Ultrafine Metals

Relatively little information exists on concentrations of ultrafine metal particles in ambient air samples away from combustion sources. There are many reasons. The ultrafine mode falls off rapidly away from the combustion source, due to the rapid migration of some types of ultrafine particles into the accumulation mode, and increased dispersion as one moves away from the source. Many sources of ultrafine metals use tall exhaust stacks, which enhances dispersion. The largest of the ultrafine particles can overlap the smallest particles of the much more abundant accumulation mode, roughly 0.2 to 0.7 μm aerodynamic diameter. Particles must be size-separated using a device with a sharp cut point, usually a multistage physical impactor, that entails problems in particle collection and analysis. Since ultrafine particles may be hard and dry, adhesive coatings are essential in order to avoid particle bounce in the impactors. Particle bounce typically translates coarser particles onto finer stages, contaminating the ultrafine particles with the enormously more abundant coarser particles. Finally, one can collect only a few monolayers of particles (at most) on the adhesive stages before particle bounce becomes important, assuming the particles themselves are not "sticky". A few monolayers of particles of 0.1 μm diameter amounts to only about 50 $\mu\text{g}/\text{cm}^2$ of total deposit. If one then desires to perform minor or trace elemental analysis of the deposit, one is then faced

with analytical requirements that reach picogram (10^{-12} gm) sensitivities. This clearly limits analytical options.

For these reasons, much of the data available on ultrafine particles does not depend on compositional analysis. Most information on the presence of ultrafine particles is derived from particle counting techniques such as the Electrical Mobility Analyzer (EMA), in situations in which the source is well known (source-enriched). This was the method pioneered in the 1972 ACHEX studies of Los Angeles (Whitby, 1978). Particle counting devices do not normally result in collection of ultrafine particles in a manner suitable for compositional analysis, although some of the devices ("particle classifiers") could be modified to provide samples for subsequent compositional analysis, if desired. The same can be argued for devices such as diffusion batteries, but to date little has been done along this line in ambient conditions.

Integrated samples of fine particles can be collected on substrates suitable for analysis. While some optical information is available as one approaches the ultrafine size, most optical techniques do not work in the ultrafine size range, which is well below the wavelength of light. A Scanning Electron Microscope (SEM) beam can still resolve ultrafine particles although some details are lost. The ultrafine particle distribution can then be derived by particle counting techniques, either manual or automated, and metal composition can be found by X-ray analysis of the single particles. The enormous gain in signal to noise ratio by selecting individual particles offsets the loss of X-ray sensitivity (typically parts per thousand) caused by use of the electron beams to induce the X rays. SEM and electron microprobe analyses rarely achieve any better than one part per thousand sensitivity. However, for single particles, this is often enough to classify them by source. Proton microprobes are, at present, not quite able to operate in the $0.1\ \mu\text{m}$ diameter region, but can perform Proton Induced X-ray Emission (PIXE) analysis to one part per million by mass on single particles as small as $0.3\ \mu\text{m}$ (Cahill, 1980).

Impactors are designed to separate particles by aerodynamic size in such a way as to allow compositional analysis. Yet here, too, ultrafine particles pose problems. First, most impactors can not operate effectively below $0.1\ \mu\text{m}$. The Stokes number for separation of a $0.1\ \mu\text{m}$ diameter particle from an air stream requires either extremely high jet velocities, extremely low pressures in the gas stream, or both. While such performance can be achieved in a physical impactor, most impactors used for ambient particle collection in the 1970's and early 1980's did not possess this capability. For example, the very popular cyclones and virtual impactors are

ineffective below about 0.5 μm diameter. The Lundgren-type impactors widely used in California studies (Lundgren, 1967; Flocchini et al., 1976; Barone et al. 1978) used 0.5 μm as the lowest cut point. Everything smaller was collected on a filter. The Battelle-type samplers (Mercer, 1964) favored by other groups (Van Grieken et al., 1975) used a lowest cut point of 0.25 μm diameter. Thus, while both these units generated copious information on aerosol composition, they could not separate ultrafine aerosols from accumulation mode aerosols.

In the mid-1980's four new impactors were developed capable of providing information on the composition of particles near 0.1 μm diameter: the Low Pressure Impactor, (LPI) (Hering et al., 1978), the Berner Low Pressure Impactor (BLPI) (Berner and Lürzer, 1980; Wang and John, 1988), the Davis Rotating-drum Unit for Monitoring impactor, (DRUM) (Cahill et al., 1985; Raabe et al., 1988), and the Multiple Orifice Uniform Deposit Impactor (MOUDI) (Marple et al., 1986; Marple et al., 1991). Battelle-type impactors were also modified to add two size cuts below 0.25 μm diameter. However, unlike the other four units, no certification of performance has been published to date on its performance in the ultrafine region. The development of reliable, clean adhesive coatings such as Apiezon™-L grease was also a major advance in the field (Wesolowski et al., 1977; Cahill, 1979), allowing separation of abundant soils from ultrafine size ranges even in dry, dusty conditions. For nominally PM-10 soils, for example, a ratio of coarse to ultrafine soils was measured at 6,600:1 at a temperatures above 30 °C and relative humidity below 20% (Cahill et al., 1985). Performances and specifications of all these units is included in a recent review paper (Cahill and Wakabayashi, 1993)

It is important to mention, however, that the motivation for development of this ultrafine capability was not for extensive studies of ultrafine metals, but rather to get a more complete picture of the accumulation mode behavior of sulfates, nitrates, organics, and other major components of the fine aerosol mix. Thus, compositional analysis was often limited to these species even when suitable samples had been collected. For example, many LPI samples were collected on stainless steel substrates, ideal for combustion analysis of sulfur, but unsuitable for analysis of transition metals by X-ray techniques.

6.9.4 Observations of Very Fine Metals

Few techniques exist for collecting particles below 0.1 μm diameter for chemical analysis. No compositional data was found for particles below 0.1 μm diameter. However, since ultrafine

particles rapidly grow into the accumulation mode, it may be assumed that measurements of the small-size tail of the accumulation mode provide some insight into the composition of the ultrafine particles. Thus, the concentration of metals in the smallest available size-cut will be examined. In order to avoid problems with definitions, particles in the smallest size-cut, which may extend to diameters above $0.1\ \mu\text{m}$, will be called "very fine" and ultrafine will be reserved for particle distributions with a mass mean diameter below $0.1\ \mu\text{m}$.

6.9.4.1 Stack and Source-Enriched Aerosols

Observation of very fine metals in source or source-enriched situations lessens problems with dilution of the sample and identification of the source. This eases both particle collection and analysis. Figure 6-96 shows the results of such a study on a coal fired power plant (Maenhaut et al., 1993) using the Berner Low Pressure Impactor (BLPI). The extreme volatilization of selenium is clearly seen, which is also confirmed in aircraft sampling of power plant stacks. Note, however, that the enrichment factor, as a function of particle size, for both sulfur and its chemical analog selenium. More refractory elements, on the other hand, are strongly enhanced in the very fine particles as compared to coarser modes.

The BLPI cuts are as follows: Stage number 1- $0.011\ \mu\text{m}$ diameter, 2- 0.021 , 3- 0.032 , 4- 0.07 , 5- 0.17 , 6- 0.30 , 7- 0.64 , 8- 1.4 , 9- 2.6 , 10- 5.5 , 11- $10.7\ \mu\text{m}$. All are for particle density $2.45\ \text{g/cm}^3$ and a temperature $120\ ^\circ\text{C}$, the conditions of stack sampling in the coal fired power plant. Both these figures were normalized to Earth crustal averages. Thus, even a two order of magnitude rise in the normalized concentration may not result in a visible "combustion mode" since the mass of soil falls very rapidly as one moves towards very fine particles. This is exactly what is predicted by the results of Natusch et al. (1974). Thus, source testing

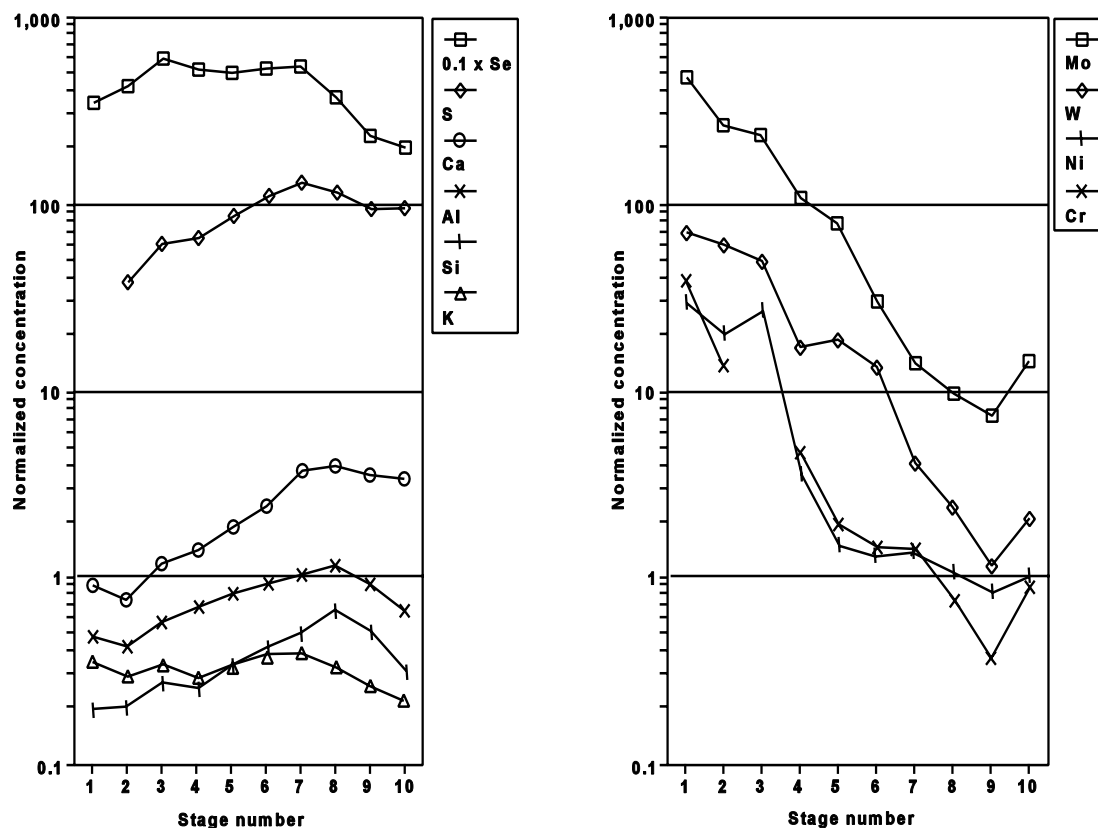


Figure 6-96. Average normalized concentrations as a function of stage number, for selenium (Se), sulfur (S), calcium (Ca), aluminum (Al), silicon (Si), potassium (K), molybdenum (Mo), tungsten (W), nickel (Ni), and chromium (Cr) for five BLPI samples from a coal fired power plant. The smallest size mode is to the left, Stage number 1, 0.011 to Stage number 11, 10.7 μm diameter. Normalization is to average crustal composition.

Source: Maenhaut et al. (1993).

confirms nucleation theory and the laboratory studies and predicts emissions of metals in the very fine particle size range from many types of high temperature combustion sources.

6.9.4.2 Ambient Aerosols

Direct Observations

Because of the difficulties in sampling and analysis, there is relatively little information on the concentrations of very fine metal particles in ambient air. Some quantitative determinations of ambient concentrations have become available in the past 15 years, however, generally as a result of a number of short but intensive aerosol studies. Examples include the extensive studies

near the Grand Canyon National Park (NP) in 1979 (Macias et al., 1981) to the Mohave Studies near the Grand Canyon NP in 1993 and the Southern is California Air Quality Study (SCAQS) in 1985-1987 (Hering et al., 1990; Cahill et al., 1990; Cahill et al., 1992a); studies at Shenandoah NP in 1991 (Cahill and Wakabayashi, 1993) and Mt. Rainier NP in 1992 (Malm et al., 1994a; Cahill and Wakabayashi, 1993), and others. While almost all of these studies used several different types of impactors with ultrafine capabilities, relatively few were analyzed for trace metal content.

An example of very fine particles persisting in ambient air is shown in Figure 6-97 using data collected at Grand Canyon NP 1984 (Cahill et al., 1987). The very fine particles behave independently from the accumulation mode, in fact often showing a net anti-correlation in concentrations of sulfur as well as dramatic differences in metals (Table 6-7). The very fine particles in Table 6-8 can be attributed to non-ferrous metal smelting activities in the region (Eldred et al., 1983; Small et al., 1981), which puts the nearest important sources a hundred miles away from the sampling site. The completely different behaviors of the accumulation and very fine particles in this arid site also show that mis-sizing by particle bounce is not significant.

Table 6-8 presents a summary of more recent data for major EPA-regulated metals (lead, nickel) and other metals, at Long Beach, CA, December in 1987 (Cahill et al., 1992a) and at Shenandoah NP in 1991 (Cahill and Wakabayashi, 1993). The elements span the range from refractory metals like nickel and vanadium to metals with low melting temperatures such as zinc and lead. These data were all taken with the same unit, the Davis Rotating-drum Unit for Monitoring (DRUM) using greased stages and a single orifice impactor (Cahill et al., 1985). The last two stages were modified from the Gand Canyon configuration as a result of theoretical and laboratory studies (Raabe et al., 1988), yielding 0.069 to 0.24 μm for Stage 8, and 0.24 to 0.34 μm diameter for Stage 7.

The DRUM data were used for several reasons: the DRUM's slowly rotating greased stages have a documented ability to handle large amounts of coarse, dry soils without contaminating the very fine stages (Cahill et al., 1985; Cahill and Wakabayashi, 1993), the elemental data are of unprecedented sensitivity for ambient very fine trace metals (PIXE and

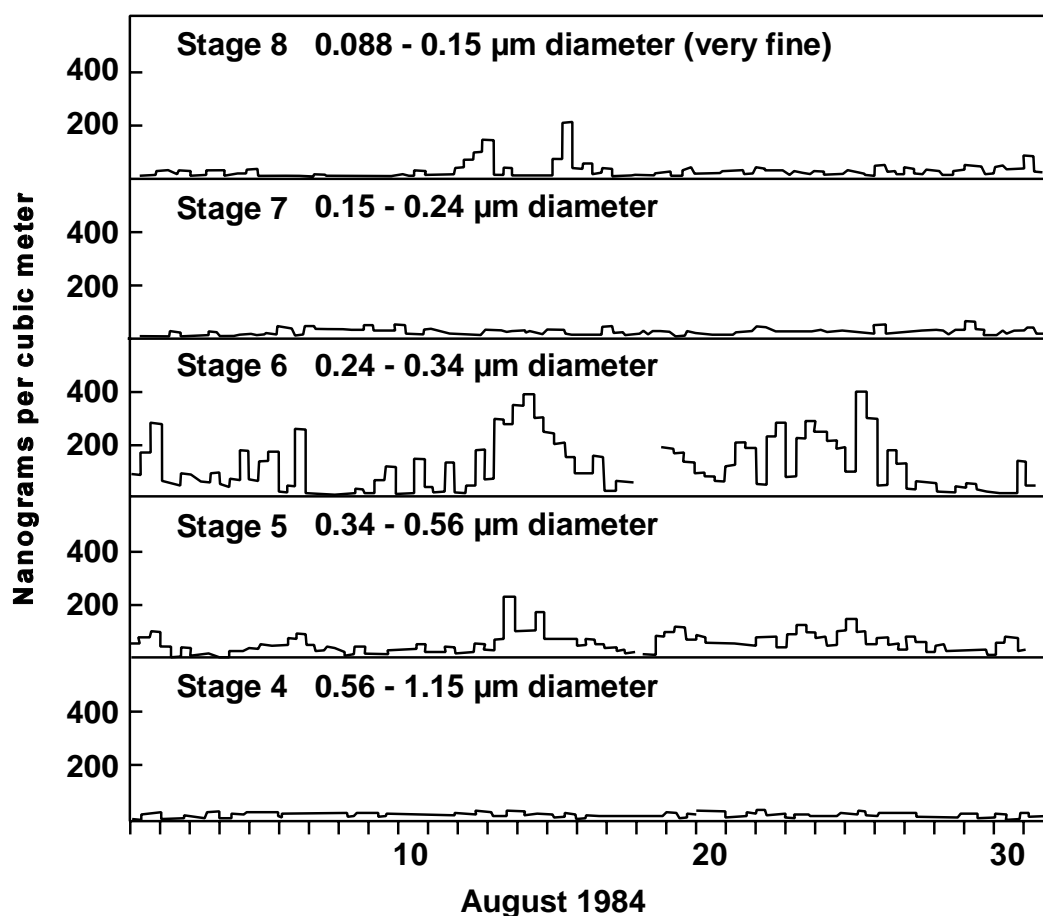


Figure 6-97. Fine and very fine sulfur at Grand Canyon National Park, summer 1984. The sulfur peaks on August 15 and August 16 were used for the compositional analysis in Table 3. The first three cut points are somewhat uncertain due to altitude and flow rate corrections. Final stage configurations are given in Raabe et al. (1988), which were used for all later studies using the DRUM.

Source: Cahill et al. (1987).

synchrotron-XRF), there is a consistency of sampler type and protocols at very different locations, and there are more trace element data from the DRUM than from any other type of unit. These advantages outweigh its disadvantages; the DRUM does not have the very fine sizing detail of either the LPI or BLPI impactor, or the ability to measure mass, ions and organic matter of the MOUDI or BLPI. The analyses were done both by PIXE and by synchrotron-XRF (Cahill et al., 1992a), with most of the trace metal data from the latter

TABLE 6-7. COMPOSITION OF THE AEROSOLS PRESENT AT GRAND CANYON NATIONAL PARK IN THE SUMMER OF 1984 FOR THE SULFATE EPISODES OF AUGUST 15 (ACCUMULATION MODE, STAGE 6) AND AUGUST 16 (VERY FINE PARTICLES, STAGE 8)

Elements	Stage 8, 0.088-0.15 μm (ng/m ³)	Stage 6, 0.24-0.34 μm (ng/m ³)
Sodium	420	10
Silicon and Aluminum	8	6
Sulfur	204	392
Chlorine	208	5
Potassium	59	3
Calcium	150	5
Titanium	2	4
Vanadium	2	3
Iron and Nickel	2	2
Copper	100	1
Zinc	931	2
Arsenic	13	2
Bromine	2	2
Lead	63	4

Source: Cahill et al. (1987).

source. In order to obtain sulfate, multiply sulfur by 3.0. These average values, however, obscure a great deal of structure as a function of time.

The variability as a function of size and time is shown in Figure 6-98 for nickel, selenium, and lead in Long Beach, CA as part of the SCAQS studies of 1987. By 1987, much of the lead was no longer automotive, and there are significant changes in the very fine fraction over periods of four to twelve hours. Note the behavior of very fine metals; almost total absence for selenium, partial absence for nickel, and constant presence for lead. Almost all elements at almost every site show similarly complex behavior. Thus, the summary of Table 6-8 can include only the most basic types of information on fine and very fine metals in the atmosphere.

TABLE 6-8. MEASUREMENTS OF FINE AND VERY FINE METALS

Site Name	Particle	Very Fine Particles					
Duration	Aerodynamic	Accumulation Mode					
Frequency	Diameters	From	From	From	From	From	From
Dates		To	To	To	To	To	To
	(D _{ae} , μm)	0.069	0.069	0.24	0.34	0.56	1.15
		0.24	0.24	0.34	0.56	1.15	2.5
		Maximum Values					
		Values					
		(ng/m ³)		Mean Values (ng/m ³)			
	Element						
Long Beach, CA							
6 days	Vanadium	6.6	2.5	6.1	10.5	12.2	8.6
6 samples/day	Nickel	3.4	1.3	4.4	7.7	4.5	0.5
(11, 12/87)	Zinc	51	17.6	46.3	140.4	189.4	39
Mean detectable	Selenium	MDL	MDL	0.32	3.0	1.4	0.65
limit - 0.3 ng/m ³	Lead	199	71.4	47.6	59.9	69.9	25.4
	Sulfur ^a		200	250	350	500	250
Shenandoah NP							
21 days	Vanadium	1.2	0.24	0.67	0.52	0.30	0.80
6 samples/day	Nickel	1.2	0.58	0.48	0.13	0.03	0.01
(9/91)	Zinc	3.8	1.42	2.16	2.60	1.92	1.66
Mean detectable	Selenium	2.7	0.14	0.11	0.52	0.35	0.14
limit - 0.15 ng/m ³	Lead	50	5.38	5.49	3.01	10.87	16.06
	Sulfur ^a		334	929	1235	1727	101

^aEstimated from graphs.

Source: Cahill et al. (1992a, 1996a).

In addition to the limited US data, comparison data have also become available from foreign sources such as from the Kuwaiti oil fires (Reid et al., 1994) and a study in Santiago, Chile (Cahill et al., 1996). While the former is a unique situation, the Santiago data are

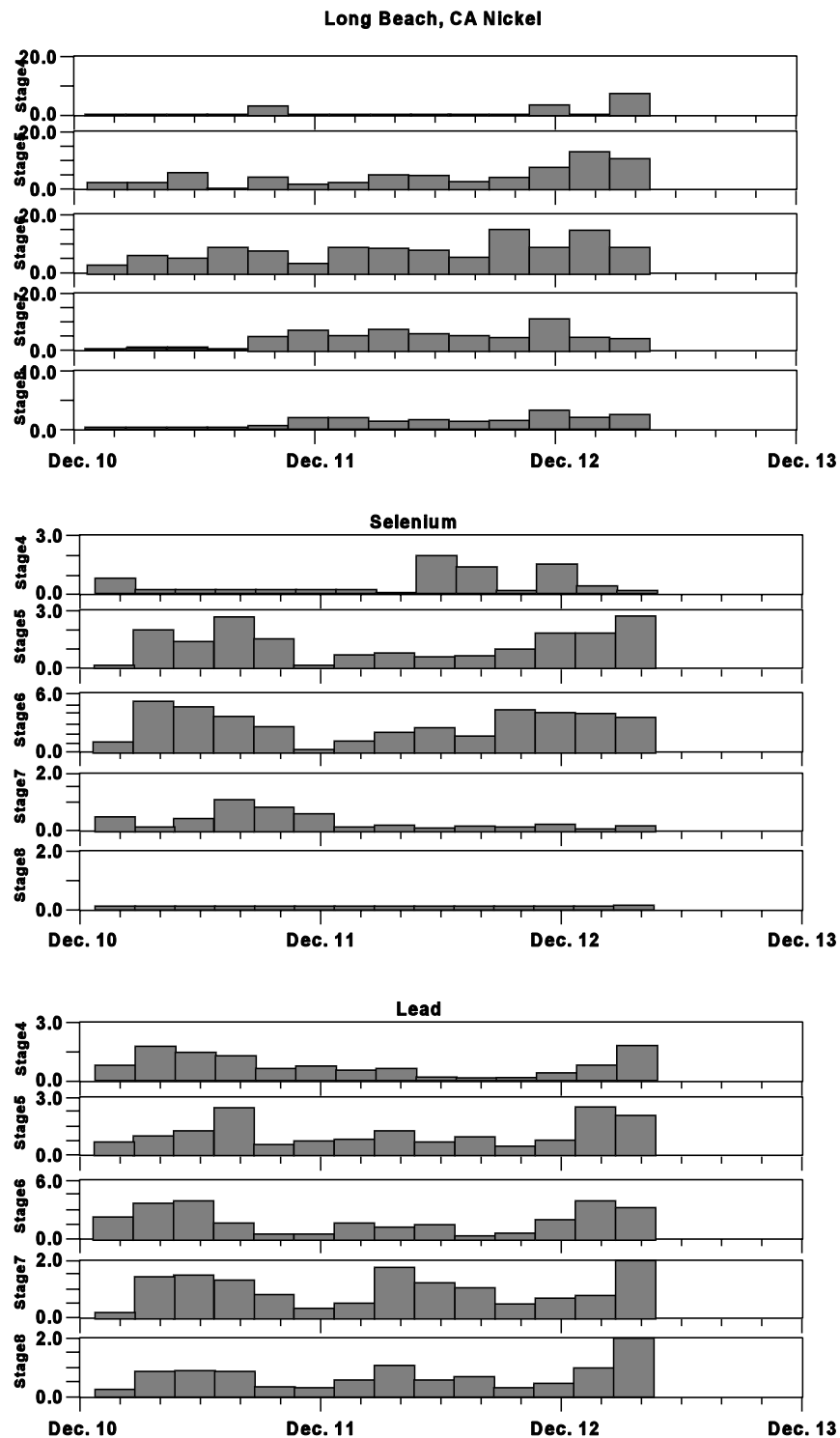


Figure 6-98. Concentration, in micrograms per cubic meter, of fine and very fine metals (nickel, selenium, and lead) in Long Beach, CA, December 10 through 13, 1987, in 4-h increments. Stage 8 is very fine, 0.069-0.24 μm ; then 0.34, 0.56, 1.15, 2.5 μm aerodynamic diameter for the upper size-cut.

Source: Cahill et al. (1992a).

especially useful since leaded gasoline is still routinely used in Chile and other countries, generating data impossible to obtain in the United States. Table 6-9 summarizes some of these data for a refractory element, nickel, and a volatile metal, lead. However, the full data set includes 450 samples of four to six hours duration, each analyzed in five fine size fractions, generally with about 20 elements found in each fraction, or approximately 40,000 individual elemental values.

Some general observations can be made from the data; first, there is an enormous variation in the concentration of fine and very fine metals, sometimes spanning 4 or 5 orders of magnitude in a few days. Such behavior can be modeled by plumes of particles that sweep over the site episodically, as opposed to area or regional sources. Second, one often finds a mixture of very fine particle or nuclei mode behavior as well as accumulation mode behavior. However, these modes may be physically separated in time.

Lead in the United States follows a variety of very different patterns. In the rural samples, lead tends to be bimodal, with a coarse component above $1.0\ \mu\text{m}$ diameter and a very fine component below $0.34\ \mu\text{m}$ diameter. This can be modeled by a very fresh fine particle mode and a coarser mode associated with resuspended soil. Urban sites, however, both in the U.S. and in Santiago, show lead in very fine particles as well as in the accumulation mode. Lead in resuspended soil is found in the coarse particle mode.

Other metals at Long Beach, however, lack a distinct concentration of very fine particles all the time (selenium) or part of the time (nickel), merely possessing an accumulation mode that closely mimics sulfates and other secondary species (Cahill et al., 1990). It is well known that nickel and vanadium were derived from high temperature combustion sources, and since each is highly refractory, they will occur primarily as very fine particles near the source. Thus, the similarity between the distributions of these elements and less refractory elements such as zinc can be understood through a rapid condensation and coagulation of the abundant secondary species around these metals, leading to an accumulation mode distribution as the secondary acidic species hydrate. Clearly, such processes are weaker at dry sites such as the arid west in summer (Table 6-8). On the other hand, Shenandoah NP has a mixture of urban and rural behavior, with occasional sharp peaks of very fine metals (nickel) superimposed on an accumulation mode behavior (sulfur, selenium) with some coarse contribution (lead,

**TABLE 6-9. MEASUREMENTS OF FINE AND VERY FINE METALS
(LEAD AND NICKEL)**

Site	Duration	Particle	Very	Accumulation Mode				
Frequency	Element	Aerodynamic	Fine					
Dates		Diameters	Particles					
			From	From	From	From	From	
			To	To	To	To	To	
			0.069	0.24	0.34	0.56	1.15	
			0.24	0.34	0.56	1.15	2.5	
			ng/m³	ng/m³	ng/m³	ng/m³	ng/m³	MDL^a
Long Beach 6 days 4 samples/ day (11/87)	Lead	Mean	71.4	47.6	59.9	69.9	25.4	0.45
		Maximum	199	95	129	164	58	
	Nickel	Mean	1.3	4.4	7.7	4.5	0.5	0.22
		Maximum	3.4	11.4	15.0	13.4	3.7	
Shenandoah NP 21 days 6 samples/ day (9/91)	Lead	Mean	5.4	5.5	3.0	10.9	16.1	0.2
		Maximum	50	20	16	70	130	
	Nickel	Mean	0.58	0.48	0.13	0.03	0.01	0.09
		Maximum	1.2	1.6	0.8	1.0	0.14	
Mt. Rainier NP 28 days 6 samples/ day (7, 8/92)	Lead	Mean	2.3	6.5	2.0	3.4	6.7	0.5
		Maximum	6	15	21	14	29	
	Nickel	Mean	Always less than MDL					0.07
		Maximum	MDL	0.4	0.8	0.4	0.7	
Santiago, Chile 14 days 6 samples/ day (9/93)	Lead	Mean	101	53	38	108	41	8
		Maximum	920	340	320	640	270	
Kuwait 14 days 4 samples/ day(6/91)	Lead	Mean	429.9	154.2	84.7	44.7	38.1	0.35
		Maximum	2580	580	128	86	70	
	Nickel	Mean	1.5	2.5	4.3	3.7	6.0	0.22
		Maximum	5	18	11	8	9	

^aMDL = minimum detectable limit at 95% confidence level, in nanograms per cubic meter

Source: Cahill et al. (1992a,b, 1996a), Malm et al. (1994a), Reid et al. (1994), Cahill and Wakabayashi (1993).

vanadium). Only through a detailed study of meteorology and knowledge of emission sources can such ambient behavior be understood.

Indirect Methods

Lacking a large body of direct data on very fine metallic aerosols, there are indirect ways to increase our knowledge of such aerosols;

1. Combustion studies have established the formation mechanism of very fine metallic aerosols, and,
2. Considerable ambient data exist that, when combined with known combustion processes, yield estimates for the concentration of very fine metallic aerosols by time and locations.
3. In conditions of low ambient concentrations of particles and low humidity, very fine particles have been shown to persist for many hours. (Cahill et al., 1985).

Thus, the numerous observations of fine ($D_p < 2.5 \mu\text{m}$) metallic aerosols in low humidity conditions can yield estimates of the presence of such metals in the very fine particles and set upper limits on their concentrations. The relatively small number of actual measurements can then serve as tests or as confirmation of our level of understanding of these biologically important aerosols. As an example, Figure 6-99 shows concentration profiles of sulfur, selenium, zinc, and arsenic, all of which can occur as very fine particles in the western United States. Arsenic and zinc are annual averages, March, 1993 to February, 1994, while the sulfur (for sulfate, times 3.0) and selenium are for summer, 1993. This was done to exhibit the correlation of these elements, which are chemically akin, during the eastern U.S. sulfate maximum each summer. The regional nature of the elements is very evident, as are certain strong sub-regional sources such as the copper smelter region of Arizona and New Mexico (arsenic).

The non-urban values shown in Figure 6-99, which are derived from the cleanest areas of the United States, are surprisingly relevant to urban areas in the same region for some of the species. Table 6-10 compares major and minor fine elements at Shenandoah NP, where there are detailed measurements of particle size, and Washington, DC, where such size information is lacking. Summer 1993 is the comparison period. Finally, two western sites are compared, both downwind of Los Angeles; San Geronio Wilderness, and Grand Canyon NP.

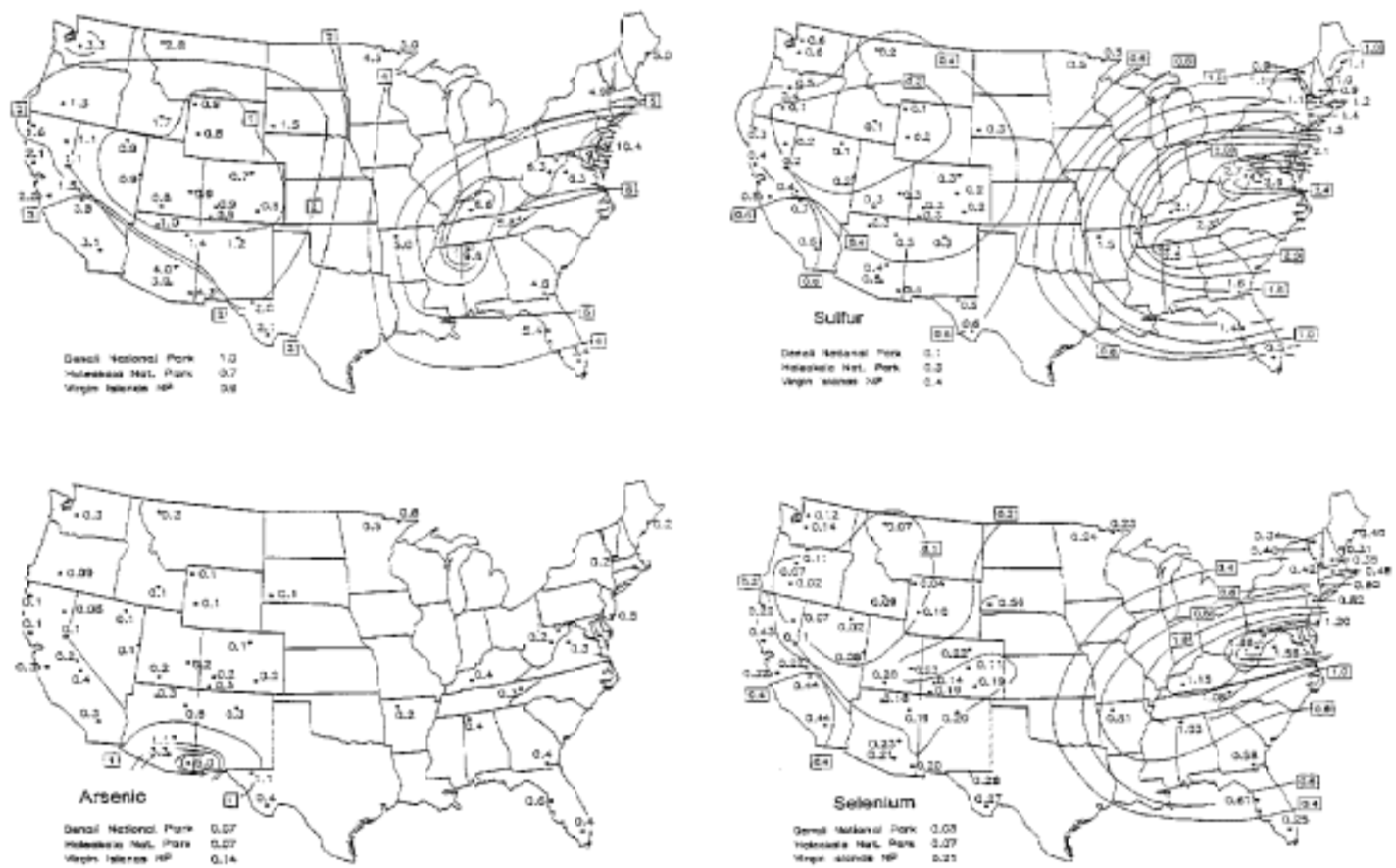


Figure 6-99. Patterns of zinc, arsenic, sulfur, and selenium in the United States.

TABLE 6-10. COMPARISON OF SELECTED SPECIES AT SHENANDOAH NATIONAL PARK; WASHINGTON, DISTRICT OF COLUMBIA; SAN GORGONIO WILDERNESS, CALIFORNIA; AND GRAND CANYON NATIONAL PARK DURING SUMMER 1993

Concentration ($\mu\text{g}/\text{m}^3$)	Shenandoah National Park	Washington, DC	San Gorgonio Wilderness	Grand Canyon National Park
Mass - PM_{10}	31.00	34.90	21.70	9.37
Mass - $\text{PM}_{2.5}$	22.50	26.50	10.30	4.50
Composition - $\text{PM}_{2.5}$				
Ammonium sulfate	11.80	14.60	2.55	1.09
Ammonium nitrate	0.40	1.47	4.44	0.25
Organic matter	2.84	5.42	3.88	1.22
Soil	1.41	1.55	0.86	0.63
Trace composition (ng/m^3)				
Nickel	0.24	0.97	0.18	0.09
Copper	1.06	3.37	0.76	0.30
Zinc	7.93	13.90	3.72	0.63
Arsenic	0.22	0.56	0.16	0.18
Selenium	1.58	2.48	0.44	0.18
Bromine	2.14	4.18	3.67	2.11
Lead	2.17	4.48	1.36	0.51
Bio-smoke tracer (non-soil fine potassium)	8.33	< 2.00	10.00	32.30
Optical Absorption ($\text{b}(\text{abs}), 10^{-6} \text{ m}^{-1}$)	19.60	41.90	13.90	5.40

Source: Malm et al. (1994b).

Inhalation of Very Fine Metals

An extensive literature exists on the deposition of fine metals in the human lung, much of which was derived from laboratory studies, some using radioactive tracer isotopes. But an example of one of the few direct measurements of lung capture of ambient very fine metals is found in Desaeleer et al. (1977) and shown in Figure 6-100. The lower cut point is only $0.25 \mu\text{m}$, but even so, the increased capture efficiency of the lung for very fine and very fine particles is clearly shown.

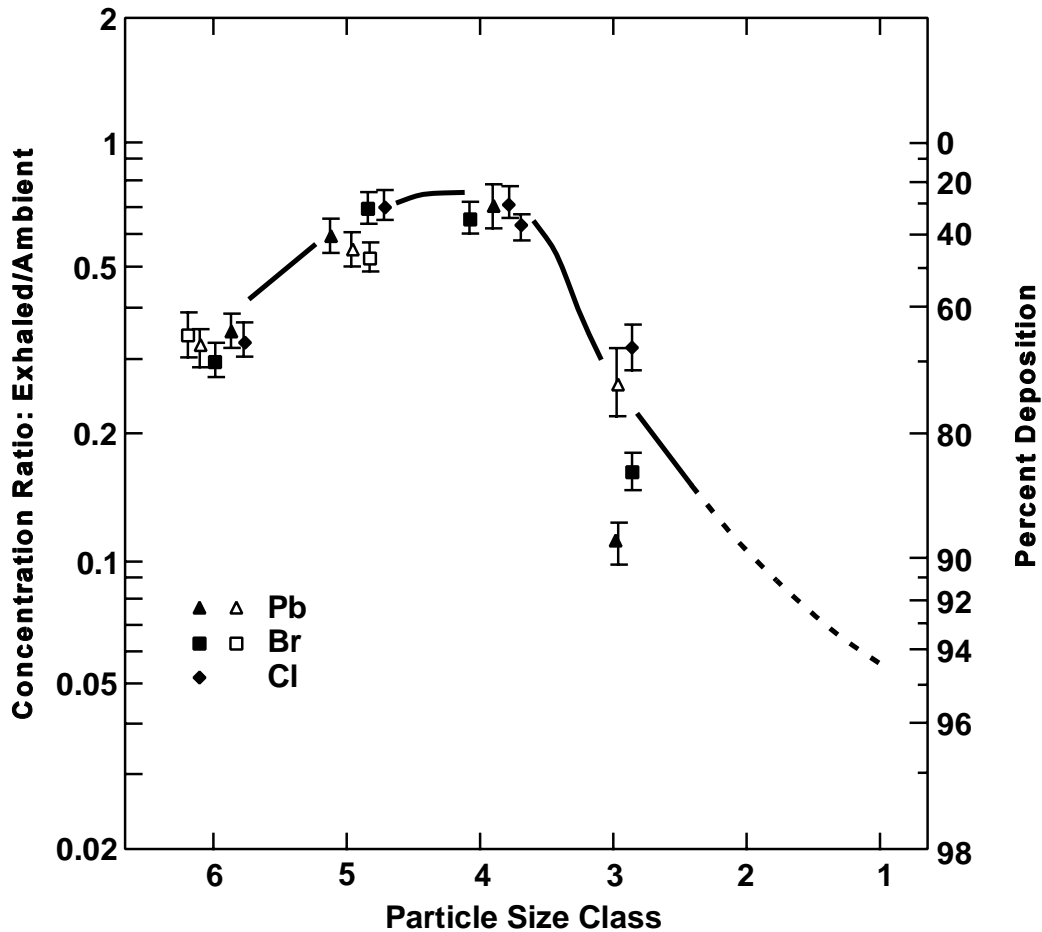


Figure: 6-100. Apparent deposition of automotive lead aerosol in the respiratory tract of one of the authors as determined by cascade impactor and Proton Induced X-ray Emissions (PIXE), as a function of aerodynamic diameter for >4, 4 to 2, 2 to 1, 1 to 0.5, 0.5 to 0.25, and < 0.25 μm particles of size classes 1 through 6, respectively. Extension of the curve to particles of diameter >2 μm (classes 2 and 1) is supported by separate experiments using chalk dust aerosol.

Source: Desaeleer et al. (1977).

6.9.5 Conclusions

There are few data on ambient concentrations of ultrafine metals. The few direct measurements can be extended with some confidence using indirect methods; i.e., particle counting techniques that have size information but no chemical information, or filter collection methods that have limited size information but detailed compositional information.